

THE SYSTEM, $\text{CaSO}_4\text{—H}_2\text{O}$.

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ABSTRACT.

Since the appearance many years ago of the investigation by van't Hoff and his associates on the various calcium sulphates and their relationships, which formed part of their classical work on the formation of the Stassfurt salt deposits, there has been an unending controversy regarding the true state of affairs in the system, $\text{CaSO}_4\text{—H}_2\text{O}$. No attempt, however, is made to give a detailed review of this literature. After considering the facts which have been brought out, and checking experimentally some that seemed most pertinent, the present investigation found that the basis for most disagreements was some erroneous suppositions regarding phase relations involving hydrated compounds. These misled van't Hoff et al. to assume that a dissociation reaction took place when they found that under certain conditions anhydrite, and, as they thought, "soluble anhydrite" also, had crystallized in solutions at the expense of gypsum. As a result of this, and the sluggishness of reaction in the case of the formation of hemihydrate, their data are erroneous.

Data brought out by various investigators, which are recounted in the text, furnish definite and reliable information regarding the system, $\text{CaSO}_4\text{—H}_2\text{O}$, between 0 and 200°. The transition point, gypsum—anhydrite, lies at $42 \pm 1^\circ$, and that of gypsum—hemihydrate at $97 \pm 1^\circ$. In the region between these two temperatures, gypsum is truly metastable. The transition point for hemihydrate into "soluble anhydrite" ($\gamma\text{-CaSO}_4$) lies apparently at a high temperature, and, owing to the instability of the two phases, cannot be established. A monotropic relation exists between anhydrite ($\beta\text{-CaSO}_4$) and "soluble anhydrite" ($\gamma\text{-CaSO}_4$).

Regarding the geologically important question of the conditions under which anhydrite may be deposited at ordinary temperatures, available information indicates that a high concentration of salt solutions is not required, but that anhydrite may be deposited from relatively dilute solutions.

INTRODUCTION.

The very extensive, though contradictory, literature which has grown around the hydrated and anhydrous calcium sulphates shows the importance and interest these compounds present, both technologically and scientifically. The most comprehensive investigation of the phases and their relationship in the system, $\text{CaSO}_4\text{—H}_2\text{O}$, was carried out almost forty years ago by van't Hoff and his associates¹ in connection with their classical work on the conditions of formation of the Stassfurt salt deposits. But despite the apparently incontrovertible evidence on which their conclusions seemingly were based, hardly a year has passed since then without the appearance of

¹ van't Hoff, J. H., Armstrong, E. F., Hinrichsen, W., Weigert, F., and Just, G.: *Z. phys. Chem.*, 45, 257, 1903; also van't Hoff, J. H.: *Bildungsverhältnisse d. ozeanischen Salzablagerungen*, Leipzig, 1912.

some paper which questioned the correctness or accuracy of one or another particular point of their investigation. More recently, Ramsdell, Partridge, and White² have reviewed and re-examined the more important questions that have been raised by various investigators, and concluded that it was necessary to modify very significantly the interpretation given by van't Hoff of the relations that exist in the system, $\text{CaSO}_4\text{—H}_2\text{O}$. They denied the individual existence of one of the solid phases ("soluble anhydrite"), and they also found important differences in values given for the transition temperatures. However, the evidence regarding the character of "soluble anhydrite" was not convincing, and besides they failed to offer any satisfactory explanation for the apparently necessary rejection of van't Hoff's experimental proofs. In view of this the controversial character was in no way removed from the interpretation of this system.

It seemed very surprising that, considering the relative simplicity of the system, $\text{CaSO}_4\text{—H}_2\text{O}$, and its accessibility for study, it could remain over a period of so many years the subject of so much controversy. Definite knowledge of the relations of the different phases appearing in this system is not only technologically important, but is also of much geological interest since in most sedimentary processes calcium and sulphate ions are present, and therefore deposition of calcium sulphate in some form is of very common occurrence. In view of this it seemed very desirable to undertake some further experiments in the hope of gaining a better understanding of this system. These experiments, carried out over seven years ago, again yielded results that could not be reconciled with van't Hoff's experimental evidence and interpretation, but as no explanation of this could at that time be found, publication did not seem warranted. The appearance recently of an article by Weiser, Milligan, and Ekholm³ proving the individual existence of "soluble anhydrite," and another by Hill⁴ on the transition point, gypsum—anhydrite, both confirming the author's results, would have made it superfluous to publish them now. But general considerations of phase relations involving hydrated compounds have led the author to conclusions which throw much light on the phase relations that exist

² Ramsdell, L. S., and Partridge, E. P.: *Am. Mineral.*, 14, 59, 1929; Partridge, E. P., and White, A. F.: *J. Am. Chem. Soc.*, 51, 360, 1929.

³ Weiser, H. B., Milligan, W. O., and Ekholm, W. C.: *J. Am. Chem. Soc.*, 58, 1261, 1936.

⁴ Hill, A. E.: *J. Am. Chem. Soc.*, 59, 2242, 1937.

in the system, $\text{CaSO}_4\text{—H}_2\text{O}$, and which show at once that much of the experimental evidence given by van't Hoff, which seemed so well founded theoretically, is in reality untenable and based on misapprehensions. In view of this, a restatement of the more important facts pertaining to the phases that enter into this system, and their relations, now seems to be justified, as it promises to bring to an end the uncertainties and controversies that have surrounded this system for so long a time.

THE SOLID PHASES.

Van't Hoff and his coworkers⁵ had accepted the existence of the following four solid phases: anhydrite (CaSO_4), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), hemihydrate ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$), and "soluble anhydrite" (CaSO_4). It is the last compound that almost from the beginning has provoked much discussion, and a number of investigators came to the conclusion that van't Hoff's "soluble anhydrite" was not a distinct and separate compound, but represented a more or less dehydrated hemihydrate. This led to the idea that the latter was "zeolitic" in its character. Ramsdell and Partridge⁶ reviewed this controversial literature, and on the basis of their own experimental evidence concluded that "soluble anhydrite" does not represent a separate phase, but is "identical in its crystal structure with hemihydrate which belongs to the zeolitic class of substances that lose and regain water of hydration without change in crystal structure." The most recent re-investigation of this subject by Weiser, Milligan, and Ekholm,⁷ however, showed conclusively that hemihydrate and "soluble anhydrite" do not have identical structures and that hemihydrate "behaves in all essential respects like a true chemical hydrate." The same conclusion was reached by the author prior to the publication of the article by Weiser et al., and as many investigations have been published disproving the individual existence of "soluble anhydrite," it is probably appropriate to present this independent evidence.

For the starting point in the investigation of this problem, the observation made long ago by Le Chatelier⁸ was used, that heating curves taken on gypsum showed two distinct breaks:

⁵ Op. cit.

⁶ Op. cit.

⁷ Op. cit.

⁸ Le Chatelier, H.: *Recherches expérimentales sur la constitution des mortiers hydrauliques*, Paris, 1887.

the first and larger one at about 128° , and a smaller break at about 163° . Le Chatelier, who was apparently the first to recognize plaster of Paris as calcium sulphate hemihydrate in composition, and its setting as a hydration process in which gypsum is formed, proved that the first break was caused by the formation of the hemihydrate, and ascribed the smaller second break to the heat effect caused by dehydration of the

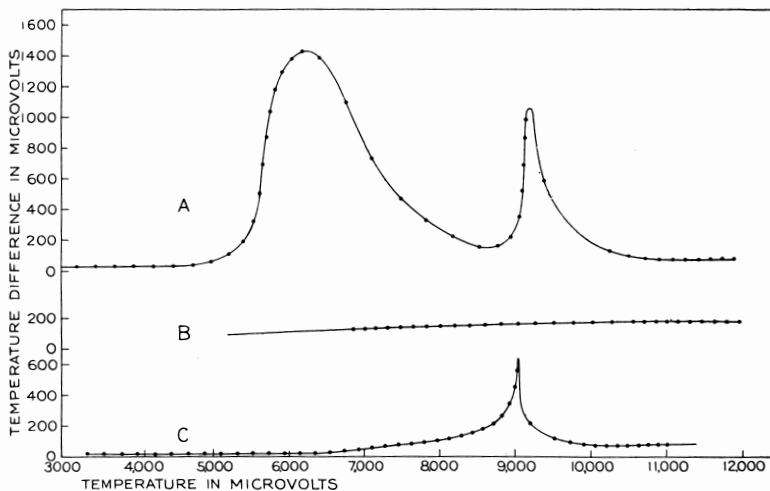


Fig. 1. Differential heating and cooling curves with a copper-constantan thermocouple.

hemihydrate. Van't Hoff stated that they were unable to verify the existence of this second heat effect, which is perhaps not surprising, considering the low sensitivity of the method when an ordinary thermometer is used, as was the case; he and his coworkers had found that anhydrous calcium sulphate was formed below the temperature at which hemihydrate formed, and for this reason attributed to retardation the effect found by Le Chatelier. It was probably this inability of Van't Hoff and his associates to duplicate the observation of Le Chatelier that led them to erroneous conclusions throughout their investigation. With thermocouples that are available at present it is easy, however, to verify the correctness of Le Chatelier's observation. In Fig. 1 is shown a typical differential heating curve, A, taken on gypsum (selenite) with a copper-constantan thermocouple. It does not matter, however, what kind of gypsum is used, the same type of curve showing

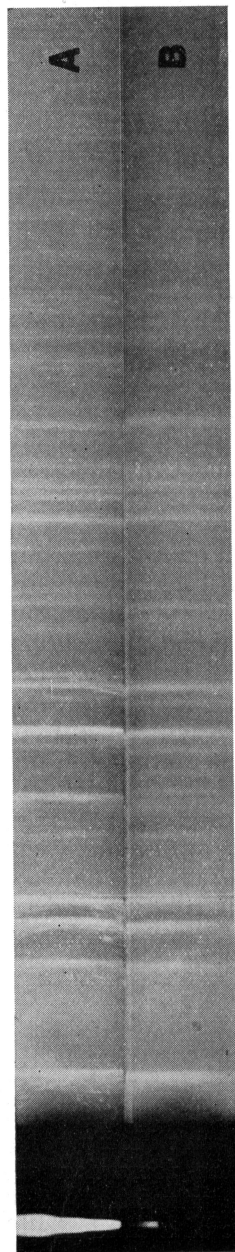


Fig. 2. X-ray diffraction: A hemihydrate, B γ -CaSO₄ ("soluble anhydrite").

two distinct absorptions of heat is always obtained, though the actual temperature of these maxima is of course considerably affected by the rate of heating, and the coarseness of the material. Below the heating curve A is shown a differential cooling curve, marked B, which was obtained on the same material right after the heating curve had been taken, and which shows no heat effects at all. The lowest curve, C, is again a heating curve on the same material after it had stood over night exposed to the atmosphere, and here a decided heat effect corresponding to the one at the higher temperature in curve A is again obtained. These curves thus give ready proof of the correctness of Le Chatelier's work, and substantiate also the criticism of van't Hoff's work by Davis,⁹ who called particular attention to the extremely rapid rehydration of the completely dehydrated gypsum when exposed to the atmosphere. The rapid rehydration explains why several investigators who did not take the necessary precautions to prevent absorption of water, and its recombination to form hemihydrate, came to conclude that the latter and "soluble anhydrite" were structurally one compound of variable composition, similar, as they thought, in behavior to zeolites. When, however, precautions are taken, important structural differences in the two substances are readily found. In Fig. 2 are shown the X-ray diffraction patterns of the two substances, taken with $K\alpha$ -radiation of molybdenum, side by side on the same film, and in Table I are given the measurements of their spacings. The "soluble anhydrite" sample in this case, after being placed in the glass capillary which was open at one end, was kept for a few hours in a furnace at about 200° , and while still hot was quickly sealed off. The data given bring out clearly the differences in the crystal structures of hemihydrate and "soluble anhydrite" and confirm in all essentials the work of Weiser and his coworkers.

Van't Hoff's statement in regard to the existence of four solid phases is therefore correct. The name "soluble anhydrite" which he introduced is a misnomer, however. Not only are there no data in existence regarding its solubility, but, as will be seen farther on, van't Hoff's notion about its solubility arose from mistaking the formation of hemihydrate in his experiments for "soluble anhydrite." As there is definite evidence¹⁰ for the existence of a third modification of anhydrous

⁹ Davis, W. A.: J. Soc. Chem. Ind., 26, 727, 1907.

¹⁰ Grahmann, W.: Neues Jahrb. Mineral. Geol., I, 210, 1914.

calcium sulphate at high temperatures—an enantiotropic inversion of anhydrite to this form is reported to take place at 1195° —it is probably desirable, for the sake of avoiding confusion, to use for the three modifications of calcium sulphate the commonly followed way of distinguishing the different

TABLE I.
X-Ray Diffraction.

Hemihydrate		$\gamma\text{-CaSO}_4$ ("soluble anhydrite")	
Spacing	Intensity	Spacing	Intensity
5.95	8	6.05	10
3.45	7	3.48	6
2.99	10	3.01	9
2.80	10	2.80	9
2.70	1	2.70	1
2.33	1+	2.33	2
2.26	0.5	2.17	1—
2.13	5	2.14	0.5
2.07	0.5—	2.09	1+
2.000	0.5	2.001	1
1.905	1	1.910	2
1.841	9	1.845	6
1.790	0.5—
1.723	2	1.738	2
1.685	4	1.690	4
1.655	3
1.605	0.5
1.526	1	1.540	0.5—
....	1.505	0.5
1.470	1	1.475	2
1.440	1	1.435	1
1.395	0.5—	1.390	0.5—
1.351	1	1.350	0.5—
1.300	4	1.297	3
1.258	3	1.264	2
1.238	2	1.237	2
1.203	2	1.211	2—
1.165	1	1.160	0.5
1.148	3	1.140	3
1.117	1
1.089	0.5	1.085	0.5
1.074	1
1.064	2
1.055	1	1.049	0.5—
1.036	1+	1.037	1
....	1.022	0.5
1.009	1	1.003	1
0.995	1—	0.992	1
0.953	0.5	0.951	0.5
0.938	0.5—
0.918	1	0.920	0.5
0.890	1	0.895	0.5

polymorphic modifications: α -CaSO₄ for the high-temperature form, β -CaSO₄ for anhydrite, and γ -CaSO₄ for the "soluble anhydrite."

THE EQUILIBRIUM RELATIONS IN THE SYSTEM, CaSO₄—H₂O,
AS DETERMINED BY VAN'T HOFF AND HIS ASSOCIATES

Establishment of the equilibrium relations between the four solid phases by van't Hoff and his coworkers rested on their determination of three dissociation pressure curves for gypsum: (1) gypsum—hemihydrate, (2) gypsum—"soluble anhydrite" (γ -CaSO₄), and (3) gypsum—anhydrite (β -CaSO₄). On the basis of these dissociation pressure curves they gave the temperature for the transition, gypsum—hemihydrate, at 107°, for gypsum— γ -calcium sulphate at 89-93°, and for gypsum— β -calcium sulphate at 63-66°. The dissociation pressures were not determined directly, however, as according to their statement, the sluggishness of the reaction in every case made it impossible to use the direct method, and for this reason they resorted to indirect ways of evaluating the dissociation pressures. For this purpose, some suitable salt solutions were utilized, which, without interacting with the solids, promoted the desired reaction presumably by increasing their solubility. Since the reaction consisted either in liberation of water, or the reverse—the taking up of water—a suitable method for observing this effect in each case was used, and the equilibrium temperature in the particular salt solution was determined. The dissociation pressure it was assumed would be equal to the vapor pressure of the solution for this temperature, and by determining the latter directly, the desired value for the dissociation pressure was obtained. By applying a thermodynamic formula it was then a simple matter to calculate from two determinations the dissociation pressure over the whole range of temperatures.

This procedure is sound, provided that a dissociation pressure actually exists, and that equilibria are definitely established, which of course van't Hoff and his associates thought they had proved to be the case. However, as will be shown farther on, they were mistaken in this, and as a result, their determinations are erroneous.

It has been mentioned above that van't Hoff and his

coworkers did not succeed in verifying Le Chatelier's experiments showing that the dehydration of gypsum proceeds always in two steps, first forming hemihydrate, which only at a higher temperature loses its water to form γ -calcium sulphate. They stated that neither by observing the temperature on heating gypsum, nor by the dilatometric method, could they find the second discontinuous change. The transition point, gypsum—hemihydrate, according to their determination was at 107° , and though in general, they said, dehydration proceeds stepwise with increasing temperature, and it would be natural, therefore, to expect further dehydration to take place at a higher temperature, certain experiments showed that gypsum changed to anhydrite below this temperature. For this reason they concluded that the upper heat effect of Le Chatelier's curve could have resulted only from delayed transformation, and further, since anhydrite was formed at lower temperature than hemihydrate when in contact with salt solutions of the same concentration, they also concluded that the dissociation pressure had a higher value. That the dissociation pressure existed was taken for granted, and neither they nor apparently any of the later investigators had given attention to the fact that it was only when a commercial plaster of Paris (or gypsum made from it) was used, that anhydrite was formed under these conditions; and that when pure gypsum was used anhydrite was not obtained. Van't Hoff et al.¹¹ said: "Wesentlich ist für das Gelingen dieses Versuches allerdings, dass nicht gewöhnlicher, z.B. präzipitierter Gips genommen wird, denn dieser zeigt auch nach mehreren Wochen nur die Halbhydratbildung. Am einfachsten gelingt derselbe, falls das Dilatometer mit Stuckgips . . . beschickt wird." In view of this it would have been pertinent to inquire why pure gypsum had not changed to anhydrite, although gypsum made from a commercial plaster (Stuckgips) was, as they concluded, dissociating directly to anhydrite. However, no attempt to find the reason for this important fact, or to give any explanation of it, was made, and, as it apparently fitted their notion of dissociation pressures, they used the behavior of this particular plaster in salt solutions to establish the dissociation of gypsum to anhydrite, and also to soluble anhydrite.

¹¹ Op. cit., p. 275.

We see, then, that the whole work of van't Hoff and his coworkers rests on the supposition (1) that gypsum can dissociate in three independent ways, each resulting in a definite dissociation pressure, and (2) that at the temperature at which the change from one solid to the other takes place in the presence of salt solutions a dissociation pressure equal to the vapor pressure of the solution must always exist. That these assumptions are not justified, except for the transition of gypsum to hemihydrate, and that even here their experiments resulted in an erroneously high temperature, will be shown farther on.

BEHAVIOR OF THE VARIOUS CALCIUM SULPHATES IN
RESPECT TO TEMPERATURE.

Gypsum, when exposed to the air at ordinary temperature, is usually stable because the partial water vapor pressure of the atmosphere is greater than its dissociation pressure. If heated to a temperature at which the dissociation pressure of gypsum becomes greater than the surrounding water vapor pressure, it begins to dehydrate. This behavior is utilized in the manufacture of plaster of Paris, that is, of the hemihydrate, from gypsum. The long experience in the manufacture of plaster of Paris presents a consistent record that whenever gypsum is heated at not too high a temperature—usually to about 130° —the product formed is invariably the hemihydrate; and further, that if the temperature is permitted to go considerably higher, the product becomes “dead burned,” it has then been converted into anhydrite. All the records of laboratory experience show that gypsum on dehydration is invariably first converted into hemihydrate, and only after this is dehydrated further to anhydrous calcium sulphate. It is clear from the discussion given earlier that this second step in dehydration results in the formation of γ -calcium sulphate, and that this is a reversible reaction. In fact, its reversibility under ordinary conditions is so rapid, owing to the low dissociation pressure of hemihydrate— γ -calcium sulphate at ordinary temperature, that some investigators have denied the existence of γ -calcium sulphate as a definite compound. With the evidence presented by Weiser et al.,¹² and confirmed in the

¹² Op. cit.

present paper, its individual existence is now well established.¹³ However, the transition point, hemihydrate— γ -calcium sulphate, has not been determined, and it is not likely that it can be determined. We know that the solubility of hemihydrate decreases very rapidly with temperature so that the dissociation pressure at the transition point practically must equal the vapor pressure of water. It would present very considerable experimental difficulties to determine this point directly, either by temperature measurements or from solubility data. But besides, as we shall see below, inversion to β -calcium sulphate takes place at these temperatures at a rate that would probably make it impossible to carry out these experiments. Therefore, all that can be said definitely about this transition is that it takes place at a temperature considerably above the transition point, gypsum—hemihydrate.

The next question of interest is the relation of β - to γ -calcium sulphate. Differential heating curves taken about 100° beyond the heat effect showing the formation of γ -calcium sulphate failed to indicate any further heat effect. The formation of β -calcium sulphate at higher temperatures is of course a well established fact ("dead burned" plaster). Therefore a few experiments were made of heating gypsum at various temperatures, and X-raying the resulting material. After a short heating at 450° , it was found to consist entirely of β -calcium sulphate. When heated at about 300° for 20 hours, the material was mostly β -calcium sulphate. After heating two days at about 250° , an appreciable amount of β -calcium sulphate besides hemihydrate was found. Even below 200° , on prolonged heating, formation of β -calcium sulphate could be

¹³ There exists, however, considerable confusion in the literature dealing with the calcium sulphates in regard to transition points and decomposition, and a few words may therefore be necessary. One meets statements to the effect that at the temperature at which gypsum is decomposed when heated in the air its dissociation pressure is equal to the atmospheric pressure; or, that because the decomposition temperature of hemihydrate found by Le Chatelier was not affected by carrying out this dehydration under reduced pressure, it was not a dissociation pressure. Such confusion may have arisen from the use of the term "boiling gypsum" ("Gipskochen") in the manufacture of plaster of Paris. Dissociation takes place whenever the dissociation pressure becomes greater than the partial water vapor pressure of the atmosphere, and reducing the total pressure has very little effect, as it is in no way similar to a boiling point. The actual temperature at which decomposition is observed on a heating curve depends much on the rate of the dissociation reaction. Unless this rate is rapid, and the experiment is carried out in a closed vessel in which the dissociation pressure would prevail, no information regarding the transition point can be obtained from a heating curve.

detected. The gradual increase in the rate of formation of β -calcium sulphate with increasing temperature, and the failure to observe any discontinuity for the heating curve on γ -calcium sulphate at a temperature where β -calcium sulphate was found to form, indicate that the relation of these two forms of calcium sulphate must be monotropic.

THE CALCIUM SULPHATES AND PHASE RELATIONS.

Gypsum, like other substances containing so-called water of crystallization, loses its water when kept in an atmosphere of sufficiently low water vapor pressure. This takes place at any temperature, but the rate of loss increases with temperature because of the rapid rise of the dissociation pressure of the hydrate. When the surrounding water vapor pressure equals the dissociation pressure of the hydrate, the latter does not lose any of its water. This whole behavior represents a reversible reaction in which, under definite conditions, exists a state of equilibrium between the hydrate on one side, and on the other the water vapor plus the substance formed when the hydrate loses this water. From the point of view of the phase rule this, or any other dissociation equilibrium, represents a two-component univariant system, that is, a three-phase system with one degree of freedom. For each temperature the two solid phases are in equilibrium with a definite vapor phase, and this vapor is the dissociation pressure. If one of the solid phases disappears, the pressure becomes changeable, as we then have a system with two degrees of freedom, and the hydrate can be in equilibrium with various pressures at a given temperature. These, however, are not dissociation pressures, but represent a range of vapor pressures within which the hydrate has a field of stability. The well-established facts in regard to all dissociation pressures show that for the existence of any dissociation pressure there must be a reversible reaction representing a univariant two-component system in which one component is volatile.

If we consider now the three dissociation pressure curves for gypsum, of van't Hoff et al., it becomes obvious from the facts mentioned above concerning the thermal behavior of gypsum that only in the case of the dissociation of gypsum to hemihydrate can the requirement of a reversible reaction that represents a univariant two-component system be met. Neither β - nor γ -calcium sulphate can form directly by removal

of water vapor from gypsum, since in the formation of β -calcium sulphate the intermediate compounds, hemihydrate and γ -calcium sulphate, intervene, and in the case of γ -calcium sulphate the formation of hemihydrate intervenes. In the presence of these intermediate compounds, the two reactions required for the dissociation curves, gypsum— β -calcium sulphate, and gypsum— γ -calcium sulphate, no longer constitute univariant systems. With the appearance of one additional phase, if this represents an equilibrium condition, the system would become invariant, and would then be a transition point—at which the three solid phases and the vapor would coexist. A change in temperature would then necessitate the disappearance of one solid which becomes unstable in the direction of the change. For gypsum to “dissociate” to either β - or γ - CaSO_4 would require the disappearance of the intermediate compounds, and since this takes place after gypsum itself has disappeared, there is therefore no possibility for gypsum to form a dissociation pressure with either β - or γ - CaSO_4 . The only dissociation pressure that can exist in this case is one for gypsum—hemihydrate.

The idea that a hydrate need not always dissociate in such a way that the next lower hydrate is formed, but may dissociate directly to some lower step, apparently gained general acceptance through the misunderstanding of an expression derived by Ostwald¹⁴ which shows the relationship of such dissociation pressures. Ostwald's assumption of a direct dissociation to that lower step, and the possibility of calculating the value of its dissociation pressure by means of his expression, seems to have been taken generally for proof of its actual existence. Such a dissociation has never been experimentally realized, however, and all reliable experimental evidence uniformly shows that, for a series of hydrates, the dissociation always results in the formation of the compound that is next in its composition. Furthermore, it can be shown¹⁵ from consideration of phase relations that the two substances which give the dissociation pressure that Ostwald had assumed, would both be unstable under these conditions, and that it would be necessary then to assume the velocity of the unstable dissociation reaction to be practically infinitely greater than the reac-

¹⁴ Ostwald, W.: *Lehrbuch d. allgemeinen Chemie*, II, 2, p. 538. W. Engelmann, Leipzig, 1912.

¹⁵ For a more detailed discussion the reader is referred to an article to be published elsewhere.

tion leading to the formation of the stable intermediate compound. For if this were not the case, and a detectable amount of the stable phase were present, the system would no longer be univariant and no dissociation pressure could exist. It may therefore be concluded that the fact that it is possible to calculate values for some assumed dissociation, from the data of related known dissociations, in no way proves this dissociation to be realizable under these conditions, or that it even need exist.

It is possible that van't Hoff mistook Ostwald's statement for proof that a substance may actually dissociate in different ways, and he doubtless assumed also, as is apparently generally assumed, that in all cases involving hydrates there must exist a dissociation pressure curve which terminates at the respective transition point. With these ideas firmly accepted, it is probably not surprising that the experiments with commercial plaster mentioned above, which showed that in the presence of salt solutions, anhydrite and supposedly also "soluble anhydrite" were formed well below the transition of gypsum to hemihydrate, led van't Hoff and his associates to believe that they had proof that gypsum was dissociating directly to either anhydrite or "soluble anhydrite" without going through the formation of the intermediary compounds. The theoretical difficulties which arise with the assumption that gypsum can dissociate in several ways apparently have not been sufficiently considered. At each transition point the dissociation pressure must then be equal to the vapor pressure of the saturated solution. But if the dissociation pressure of gypsum were equal to the vapor pressure of the solution at its transition to anhydrite, it must beyond this point become greater than the vapor pressure of the solution, as otherwise no transition could take place. At the transition point to hemihydrate, at the higher temperature, gypsum, however, must again have a dissociation pressure that is equal to the vapor pressure of its solution. It is not only theoretically necessary, but also a well-established fact, that the vapor pressure of such solutions increases with temperature, irrespective of whether the solubility of the solid phase (binary compound) increases or decreases with the temperature, as that can affect only the slope of the vapor pressure curve.¹⁶ How, then, can the same gypsum have a dissociation pressure equal to the vapor pressure of its saturated solution at the upper

¹⁶ The only exception to this takes place when the solubility curve passes through the congruent melting point of the solid, after which the vapor pressure decreases, but such a case does not enter the present discussion.

transition, when even at the much lower temperature, after passing its transition to anhydrite, it had to develop a dissociation pressure that surpasses the vapor pressure of its solution? The ability to realize the higher transition would require that the dissociation rate for the lower one be infinitely small. It would further require one to assume that, though dissociation usually increases very rapidly with temperature and had to have a higher absolute value, in this case, it still must remain undetectable at the upper transition point, for otherwise the latter could no longer be an invariant point. It seems necessary to conclude either that the lower transition point would never be attainable, or that the upper transition could never be realized, and that actual realization of both transitions based on the dissociation of gypsum is impossible.

The proof that gypsum dissociated directly to anhydrite was thought by van't Hoff and his associates to be furnished by experiments in which gypsum made from commercial plaster of Paris in the presence of salt solutions was converted to anhydrite at temperatures below the transition point of gypsum—hemihydrate. But these experiments prove directly only that the transition gypsum—anhydrite takes place at a lower temperature than the transition gypsum—hemihydrate, and that, therefore, anhydrite above its transition point with gypsum is the stable phase in the system, CaSO₄—H₂O, and hemihydrate and "soluble anhydrite" are unstable phases. The solubility of a stable phase is lower than that of an unstable phase, and therefore if both are brought together in contact with solution, the stable will grow at the expense of the unstable. This process generally consists in that the unstable goes into solution, and from the supersaturated solution the stable phase crystallizes out. Gypsum shows a perfectly normal behavior, that is, its solubility is considerably greater than that of anhydrite above their transition point, and therefore crystallization of the stable phase would take place through the medium of solution.

It should be recalled that van't Hoff and associates said that ordinary gypsum, after standing for weeks in contact with salt solutions, never changed to anhydrite, but only to hemihydrate, and that it was essential for the supposed dissociation to anhydrite to use a commercial product. The reason why ordinary gypsum in salt solutions is readily dehydrated to hemihydrate is that its dissociation pressure is lower than the vapor pressure of the salt solutions. On the other hand, in the case

of anhydrite when the commercial product was used, no dissociation need have taken place but a recrystallization through the medium of solution, owing to the presence in this material of nuclei of the stable anhydrite phase, for otherwise, suitable preparations of gypsum, of unquestionable purity and homogeneity, would easily have been found to show similar behavior, and that was clearly not the case. Experiments made by the writer in this connection showed that gypsum had not changed in contact with its solution at 75° after two years, but in a parallel experiment where a small amount of anhydrite had been added, the solid, as would be expected, was found to consist only of anhydrite. Further, X-ray examinations of two commercial plasters of Paris showed in both cases easily detectable amounts of anhydrite, and it seems more than probable that all commercial products would contain at least some nuclei of anhydrite. Obviously, then, the experiments of van't Hoff et al. present no direct proof for the ability of gypsum to dissociate to anhydrite directly, but are based purely on the assumption that such a dissociation pressure should exist, and their experimental work is based entirely on this assumption. As would be expected, it is exceptionally well reasoned, and appears therefore very convincing, but a closer study indicates ample opportunities for delusion. Their data were obtained from measuring very small dilatometric changes which, over long periods of time, were only indicating the trend of the supposed dissociation reaction. Van't Hoff and his coworkers apparently did not consider that besides the formation of anhydrite in their dilatometer, hemihydrate would no doubt also be formed by dissociation of gypsum in the salt solutions; and it is probable that it was the reversibility of this reaction that was indicated by the observed trends of the dilatometer readings, which they took as proof of having approached equilibrium from both directions in the supposed dissociation of gypsum to anhydrite. Their determination of this transition point is clearly not well founded, and the dissociation pressure curve when gypsum goes over into "soluble anhydrite" (γ - CaSO_4) is obviously erroneous. We have mentioned already the ease with which γ - CaSO_4 takes up water from the atmosphere, and changes to hemihydrate. It may now be added that γ - CaSO_4 has recently been found to be a more efficient drying agent than concentrated sulphuric acid,¹⁷ and

¹⁷ Hammond, W. A., and Withrow, J. R.: *Ind. Eng. Chem.*, 25, 653, 1933; Bowers, J. H.; *Bur. Standards J. Research*, 12, 241, 1934.

it remains effective even at 100° . Obviously, then, it is impossible that the transition point, gypsum— $\gamma\text{-CaSO}_4$, could lie at 93° and a vapor pressure of 588 mm., as was found by van't Hoff and his coworkers. Like some other investigators, they had probably mistaken the formation of hemihydrate in their salt solutions for $\gamma\text{-CaSO}_4$.

As unfounded as the assumption of the possibility to realize for a substance different dissociation reactions under the same thermodynamic conditions is the notion that a dissociation pressure curve must terminate at every transition point involving a hydrate. According to the phase rule, the transition point in a two-component system is a quadruple point—a point at which two solid phases coexist with their saturated solution and the vapor phase. Thus every intersection of two solubility curves forms a transition point. Only when between the two solids and the vapor there exists a reversible reaction resulting in the formation of a univariant system, is the transition point the locus of an actual dissociation pressure curve. When this is the case, the transition point is an incongruent melting point, as the dissociation pressure at this point becomes equal to the vapor pressure of the solution saturated in respect to both solids, and therefore formation of the liquid phase at the expense of the higher hydrate must take place. But not every transition point involving a hydrate need necessarily be an incongruent melting point, as seems to be generally assumed. When, as in the present case, the two solids cannot form with vapor a univariant system, because of formation of one or more intermediate reaction products, no dissociation pressure curve can terminate at their transition point. For this reason no incongruent melting takes place, and the change from one to the other solid goes through the medium of solution. This type of transition will always be met when, besides a hydration series in which the individual members originate directly from one another by loss of water, there exists in the same system also a compound (or another series) which is probably in its structure essentially different, and is linked with the first by some form of polymorphism.

SOLUBILITY OF THE SOLID PHASES IN THE SYSTEM,
 $\text{CaSO}_4\text{—H}_2\text{O}$, AND THEIR RELATIONS.

The above conclusions regarding the existence of two distinct types of transition points, which may be encountered when

dealing with hydrates, show that only in the case of one of them does a dissociation pressure curve terminate at this point, and can be used for its location. In the other type no dissociation reaction exists, and the only way to locate the transition point of the two solids is by the generally applicable method of determining the intersection of their solubility curves. The transition point, gypsum—anhydrite, is of this second type, and this is the reason why van't Hoff's vapor pressure experiments led to an erroneous result.

The solubility of gypsum has been very carefully determined by Hulett and Allen,¹⁸ who found that the values given by most earlier investigations were too high, owing to supersaturation resulting from small particle size. In an earlier paper, Hulett¹⁹ showed that solubility values for gypsum may be as much as 20 per cent too high when extremely finely divided material is used, and therefore they carried out their solubility determinations on gypsum using plates of selenite which were freed from fine particles by washing, and to avoid abrasion they stirred only the solution above these gypsum plates. Since this procedure could not be followed throughout the present investigation, it was desirable to determine what differences may be found when ordinary powdered material is used, and the saturation of solutions carried out in the usual way by turning the bottles in the thermostat. Preliminary experiments gave high solubility values which, however, were found to be caused by faulty filtration when Gooch asbestos filters were used. It seems possible that some of the high values obtained by earlier investigators were not always caused by supersaturation, but by the taking, in some cases, of samples without filtration of apparently perfectly clear settled solutions, which the present experience shows may hold some of the very fine particles in suspension. When silica filters of fine porosity were used in filtration the difficulty appeared to be removed, and solubility values were obtained which below 50° were identical with those given by Hulett and Allen. It seems, therefore, that while fine particles may no doubt cause considerable supersaturation, abrasion from turning the bottles is not serious, and the rate of recrystallization of gypsum is high enough to permit the establishment of correct solubility values, provided sufficient time is allowed for attaining equilibrium. The solubility values above 50° were found consistently to be

¹⁸ Hulett, G. E., and Allen, L. E.: *J. Am. Chem. Soc.*, 24, 667, 1902.

¹⁹ Hulett, G. E.: *Z. phys. Chem.*, 37, 385, 1901.

about 3 per cent higher than those of Hulett and Allen. Their solubility value for gypsum at 100° is practically identical with that for hemihydrate, which, as we shall see below, is the stable phase at this temperature. It seems certain, therefore, that equilibrium had not been attained, and the solution, at least in this case, had not reached saturation. That gypsum in contact with its solution was converted at 100° to hemihydrate was first stated by Davis,²⁰ and more recently confirmed by Partridge and White.²¹ This directly contradicts the statement made by van't Hoff and his associates that hemihydrate was not formed from gypsum in boiling water, and that their transition point lies at 107°. Although they arrived at this temperature by an indirect method, their experiments seemed very precise and convincing, since they showed that equilibria were approached from both sides. In view of the importance of obtaining certainty regarding this point, and the ease with which it can be checked, the experiment was again repeated. Coarsely powdered selenite was heated with water in a flask, provided with a condenser, on an electrically heated air-bath. Provision was made to prevent superheating, and readings of the temperature of the solution were no higher than 100.5°. Within about two days the gypsum had been completely converted at this temperature into needle-like crystals of hemihydrate that were about 2 mm. in length. Their growth during this time, and the disappearance of gypsum could readily be observed. The crystals were separated by quickly pouring off the solution, followed by washing them off with acetone, and were readily identified as hemihydrate. The repeated confirmation of the formation of hemihydrate from gypsum at boiling temperature shows the statement of van't Hoff and his associates to be untenable. It is necessary to accept the conclusion that, despite the apparently excellent experimental evidence, showing high precision, van't Hoff's indirect determination of the transition of gypsum to hemihydrate resulted in too high a value.

Partridge and White²² determined the solubility curve of hemihydrate from 98 to 200°, and pointed out that the data given by Hall, Robb, and Coleman,²³ as well as earlier investigators whom they cite, though mistakenly ascribed to "soluble

²⁰ Davis, W. A.: *J. Soc. Chem. Ind.*, 26, 727, 1907.

²¹ *Op. cit.*

²² *Op. cit.*

²³ Hall, R. E., Robb, J. A., and Coleman, G. E.: *J. Am. Chem. Soc.*, 48, 927, 1926.

anhydrite," are in excellent agreement with their values. From the intersection of the solubility curve of hemihydrate with that of gypsum, they gave the transition point as 98° , and by using the solubility data for gypsum given in the present paper, the intersection, as shown in Fig. 2, is found only half a degree lower. The temperature of $97^{\circ} \pm 1^{\circ}$ for the transition point, gypsum—hemihydrate, can be considered securely established.

Partridge and White also determined the solubility of β - CaSO_4 (anhydrite) between 100 and 200° , and making use of a determination by G. L. Haddon and M. W. A. Brown at 33° , concluded that the transition point, gypsum— β -calcium sulphate, lies near 40° and not at 63 – 66° as given by van't Hoff. In a very recent paper, Hill²⁴ gives the solubility of β - CaSO_4 for several temperatures below 100° , and finds that a curve put through these points intersects the solubility curve of gypsum at 42° . He calls attention to the fact that even when a long period of time—four months—is allowed for reaching equilibrium, solubility determinations may differ as much as 5 per cent, depending on whether the approach is made from supersaturation or undersaturation, the former giving high and the latter low values. The data of Partridge and White for the solubility of anhydrite between 100 and 150° are consistently lower than those given by Hall, Robb, and Coleman, but at higher temperatures practically identical values were obtained in both investigations. The time allowed for coming to equilibrium was in both relatively short—mostly less than twelve hours. The agreements at higher temperatures suggest that attainment of equilibrium was probably facilitated at these temperatures by the greater rate in recrystallization, and therefore also of solution. At lower temperature more time may be expected to be required for this, and low values may be caused by insufficient time to reach saturation when coarsely crystalline material is used, while high values may possibly result from insufficient time for recrystallization of some very fine particles, which, if fine enough, may pass through the filter when samples are taken. Experience gained in determining solubility of gypsum mentioned above strongly indicated the latter possibility. In the present experiments, differences in solubilities under apparently identical conditions were found for various samples of anhydrite. Coarsely crystallized natural anhydrite gave low values, and the solubility values for artificial anhydrite, made by heating gypsum, were usually

²⁴ Hill, A. E.: J. Am. Chem. Soc., 59, 2242, 1937.

higher, the lower the temperature to which it had been heated. It was thought that anhydrite made at low temperatures, though aggregated, would consist of very fine primary particles, which may readily disperse in solution and then pass through the filter, giving apparent higher solubilities. This, however, was not definitely established, and since the differences were not great enough to cause any uncertainty in locating the solubility curve

TABLE II.
Solubility Determinations.

Expt.	Temp. °C.	Time	Grams CaSO_4 per 100 grams H_2O	Starting materials
<i>Solid phase: gypsum</i>				
23	0	10 days	0.175	Gypsum ¹
21	24	7 days	0.207	"
18	24	11 days	0.207	"
36	38	2 days	0.210	"
36a	38	3 days	0.210	"
19	50	8 days	0.208	"
22	50	10 days	0.208	"
44	51	1 year	0.209	"
45	51	1 year	0.206	"
35	60	15 days	0.202	"
38	60	15 days	0.203	"
47	72	2 years	0.198	Selenite ²
48	72	2 years	0.198	"
32	75	22 days	0.192	Hemihydrate ³
41	92	13 days	0.175	Gypsum ¹
41a	92	23 days	0.179	"
<i>Solid phase: hemihydrate</i>				
26	100.5	2-3 days	0.160	Selenite ²
<i>Solid phase: anhydrite</i>				
28	26	11 days	0.253	Anhydrite ⁴
52	30	10 days	0.243	Natural anhydrite ⁵
53	37	6 days	0.219	"
54	37	7 days	0.234	Anhydrite ⁴
39	47.5	17 days	0.199	"
37	60	13 days	0.156	"
50	72	2 years	0.136	"
58	85	1 year	0.105	Anhydrite ⁴ and small amount of selenite ⁴
56	85	1 year	0.103	Anhydrite ⁴
42	92	29 days	0.091	"

¹ J. T. Baker, calcium sulphate, C.P.

² Clear plates of selenite, Wayne County, Utah.

³ Made from selenite by heating with water at 100.5°.

⁴ Made by heating gypsum a few hours at about 500°.

⁵ Anhydrite from Midland, California.

for the purpose of the present investigation, only attempts to minimize the possible differences were made, by allowing long periods of time for reaching equilibrium, and by using sintered silica filters of fine porosity for taking samples.

As in the determinations of the solubility of gypsum, samples of solutions were always taken at the temperature of the experiment. After allowing a short time for the solid to settle, the

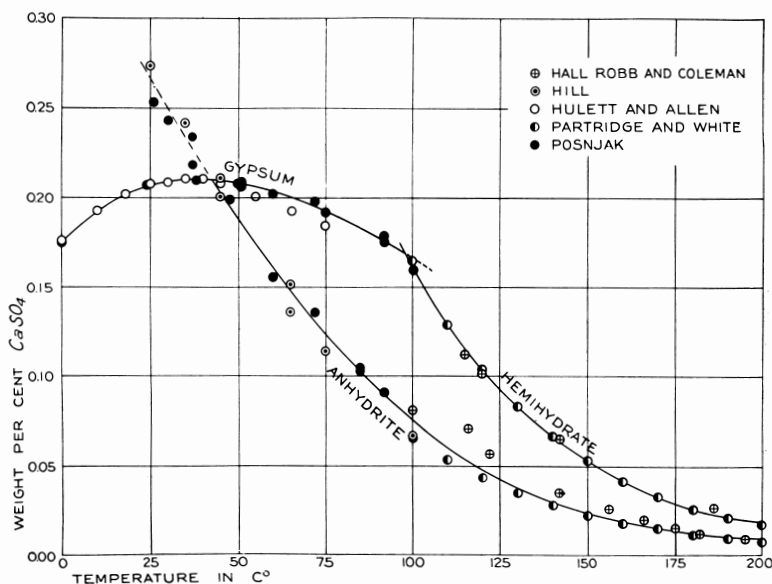


Fig. 3. Solubility of gypsum, hemihydrate, and anhydrite.

stopper of the bottle was replaced quickly by one enclosing the stem of a small immersion filter which was connected to the stopcock of an evacuated bottle. By opening the stopcock the desired amount of solution was slowly sucked into the evacuated bottle. The experimental data are given in Table II. In Fig. 3 the solubility values for anhydrite obtained in all the investigations mentioned above are shown, and, as will be seen, they lie close around a curve that intersects the solubility curve for gypsum at 42°, the temperature given by Hill for the transition point, gypsum—anhydrite, and this temperature is probably correct well within two degrees.

In regard to the transition point, hemihydrate— γ -calcium sulphate, and the solubility of γ - CaSO_4 no definite informa-

tion is available. The ease with which $\gamma\text{-CaSO}_4$ takes up water vapor to change to hemihydrate shows that the dissociation pressure is very low, and that their transition point lies probably at a fairly high temperature. Attempts made to determine this dissociation pressure curve by direct measurements were unsuccessful, owing to their instability: even below 100° , formation of anhydrite was found to take place slowly, and no reliable values could be obtained, as the requirement for dissociation of a three-phase system was no longer fulfilled.

CONCLUSIONS REGARDING THE DEPOSITION OF ANHYDRITE.

The fact that anhydrite does not form directly from gypsum by dissociation, and that their transition temperature is therefore not affected by the vapor pressure of solutions with which they may be in contact, but is governed by their solubilities, has a geological significance in the interpretation of the conditions of their deposition from sea water. The effect of the presence of salt solution, with which it is of course assumed calcium sulphate does not directly react, on the transition temperature of gypsum to anhydrite will depend on the change in the solubilities of the two solids in such solutions. Three possibilities may be foreseen to result from the presence of salts in the solution. The first is when the solubility of each is either increased or decreased in a relatively equal amount, and their transition temperature will be left unaffected. The second is when the solubility of gypsum is increased relatively more than that of anhydrite, and this will result in lowering the transition temperature. The third possibility, which, however, is probably less likely to take place, appears when the solubility of anhydrite is increased relatively more than that of gypsum, resulting in a raising of the transition temperature. It should be noted that it is the relative change in the solubility of the two solids, and not the absolute amount that is important in affecting the transition temperature. Furthermore, it may be pointed out that in general the angle of the two intersecting curves is of much importance, as it determines how much the transition temperature will be affected by a relative change in the two solubilities. Even a small change in the relative solubilities may therefore produce a surprisingly large effect on a transition temperature.

No data are available for the solubilities of gypsum and anhydrite in sea water at various temperatures. It is known,

however, that the presence of sodium chloride increases the solubility of calcium sulphate very much. On the other hand, sulphates decrease the solubility because of the effect of the common ion. Hill²⁵ determined the solubilities of gypsum and anhydrite in three concentrations of potassium sulphate—from zero to 0.12 per cent—at 35°, and, as the values for each lie on a straight line, he used them to extrapolate the solubilities in pure water. These lines are not parallel, as will be seen from Fig. 4, where Hill's data are plotted, but show that in potassium sulphate solutions the solubility of anhydrite is more

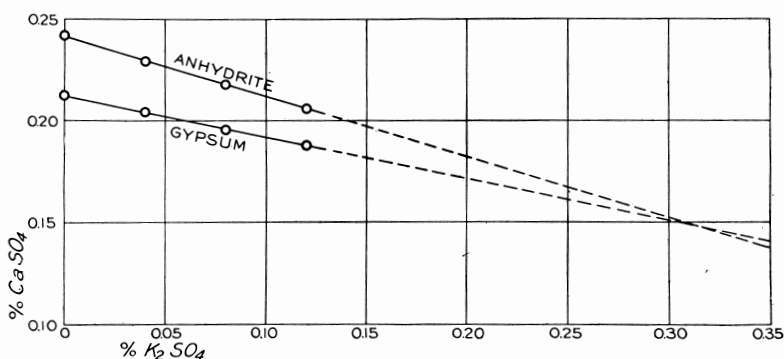


Fig. 4. Solubilities of gypsum and anhydrite in solutions of K_2SO_4 at 35° from data of A. E. Hill.

repressed than that of gypsum. When these lines are extended beyond the experimental data to higher concentrations of potassium sulphate, as shown in Fig. 4, it is found that they will intersect when the solution of K_2SO_4 reaches a concentration of 0.32 per cent. This intersection shows, of course, that in a solution of the above concentration of K_2SO_4 the transition temperature has been lowered about 7° to the temperature of 35°. The vapor pressure of the solution is only insignificantly lowered by the additional amount of dissolved material, and this therefore shows the effectiveness of only a small change in the relative solubilities of gypsum and anhydrite on their transition temperature. It is probably not unreasonable to expect a considerable lowering, which may possibly bring the transition down to ordinary temperature, to take place in sea water.

²⁵ Op. cit.

Solubility experiments in sea water to ascertain definitely the effect on the transition point are now under way.

According to the data collected by the *Challenger* expedition, the salinity of the waters of the open ocean is very uniform. Considerable differences, however, are found in basins such as the Baltic where the large inflow of fresh water lowers the salinity, and on the other hand, the Mediterranean and the Red Sea, which are nearly enclosed, and where a high rate of evaporation combined with the absence of the inflow of fresh water markedly raises the salinity. Ocean water is not saturated in respect to calcium sulphate, and bottom samples collected by the *Challenger* expedition showed that no deposition of calcium sulphate normally takes place. Thick beds of gypsum and anhydrite of marine origin are common, however, and in the Stassfurt salt deposits anhydrite reaches a thickness of almost 100 meters. The amount of calcium sulphate is entirely out of proportion to its presence in sea water, and van't Hoff²⁶ pointed out that the large amount of anhydrite in Stassfurt could not be accounted for by the evaporation of sea water, but that inflow of calcium sulphate-rich water must be assumed. Geologists considered intermittent replenishment of the water in the evaporating basin, and advanced the so-called bar theory. While this might account for the accumulation of thick deposits, it in no way explained the formation of the anhydrite beds, as long as it was assumed that anhydrite could form only from highly concentrated salt solutions. Apparently it is well known that calcium sulphate is precipitated at ordinary temperature long before the solution reaches such high concentration of sodium chloride. If so, the solubility of calcium sulphate, after first increasing with increasing concentration of sodium chloride, reaches a limit, and may be expected to decrease with further concentration. Whether gypsum or anhydrite will be deposited when saturation for calcium sulphate is reached at a given temperature depends on which will then be less soluble. From the foregoing it is probable that high concentration of salts will not be required to bring the deposition of anhydrite down to ordinary temperature. It is expected that solubility determinations in salt solutions will indicate definitely the ranges of temperature and concentration under which either gypsum or anhydrite may have been deposited from sea water.

²⁶ van't Hoff, J. H.: Zur Bildung der ozeanischen Salzallagerungen, II, p. 42 and p. 72, Braunschweig, 1909.

SUMMARY.

It is confirmed that γ -CaSO₄ (suggested for the misnomer "soluble anhydrite") is a definite chemical compound which takes up moisture very readily to change to CaSO₄· $\frac{1}{2}$ H₂O (hemihydrate). The only other two solids existing in the system between 0 and 200° are CaSO₄·2H₂O (gypsum) and β -CaSO₄ (anhydrite).

The assumption of van't Hoff and associates that gypsum may dissociate in three different ways, forming hemihydrate, anhydrite, or γ -CaSO₄, is shown to be erroneous. Gypsum can dissociate only to form hemihydrate, and their transition point, based on new determinations of the solubility of gypsum, lies at $97.5 \pm 1^\circ$, confirming the work of Partridge and White.

No dissociation pressure curve terminates at the quadruple point, gypsum—anhydrite, which results solely from the intersection of their solubility curves. The temperature of this transition point given recently by Hill at 42° has been confirmed by additional solubility determinations.

Owing to the fact that the only dissociation pressure curve that gypsum has does not reach the value of the vapor pressure of its saturated solution until the temperature of $97 \pm 1^\circ$ is attained, gypsum in contact with its solutions between 42 and 97.5° represents a true metastable system, which in the absence of anhydrite nuclei may persist indefinitely.

The effect of salt solutions on the transition temperature of gypsum to anhydrite is discussed. Contrary to former assumptions, it is shown that the presence of even a very small amount of salt in the solution may lower this temperature considerably. The importance of this fact in geological interpretations of formation of anhydrite of marine origin, and the need of quantitative data for its evaluation are pointed out.